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DEVELOPMENT OF WATERLESS HAND CLEANER

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DEVELOPMENT OF A WATERLESS HAND CLEANER.

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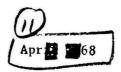
Theodore Kapala George J. Merritt

for

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Clothing and Organic Materials Laboratory U.S. ARMY NATICK LABORATORIES Natick, Massachusetts 01760

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FOREWORD

The Office of Civil Defense (OCD), Department of the Army, has experienced product separation and failure of the container in the storage of waterless hand cleaners procured in accordance with Federal Specification P-H-31a. At the request of that office, the U.S. Army Natick Laboratories (NLABS) has developed a compound having good cleaning and bactericidal properties. This cream is formulated to withstand storage conditions of -40°F to 160°F without separation. A leakproof container having a minimum 5-year storage life is proposed. Paper towels for removal of soil and excess cream are also recommended for inclusion in the OCD Sanitation Kit.

Many of the products compared for their efficacy with this hand cleaner were of commercial origin. However, they were not developed or manufactured to meet Government specifications, or to withstand the tests to which they were subjected.

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ABSTRACT

A waterless hand cleaner has been developed by the U.S. Army Natick Laboratories for inclusion in the Civil Defense Sanitation Kit. This sanitation kit, which is described in Part D, Chapter 2, Appendix 1 of F.C.D.G. entitled "Description, Storage and Handling of Public Fallout Shelter Supplies and Equipment", has an estimated storage life of more than five years. The contents of this kit must satisfy the sanitary requirements of occupants in Civil Defense shelters. The cleaner developed under this study to replace the current product is a paste emulsion of a mineral oil, a hydrocarbon solvent, an amine soap, a humectant, an anionic surfactant, a protective colloid, and a germicide, hexachlorophene, which has microbial-inhibitory properties. The cleaner shows good soil removal properties and good storage stability properties at room temperature as well as at -40°F. or -26°F. and 155-160°F. A key-opening band, reclosure-type round can made of hot dipped tinplate or 0.50 pound minimum electrolytic tinplate is recommended for packaging the cleaner. The seam-sealing compound must be inert both to the cleaner and the solvent.

DEVELOPMENT OF A WATERLESS HAND CLEANER

1. Introduction

At the request of the Office of Civil Defense (OCD), Department of the Army, the U.S. Army Natick Laboratories (NLABS) initiated a study in 1966 to develop an effective waterless hand cleaner that would be stable during storage in unheated shelters, active bactericidally, and in-irritating to the skin. The study was conducted at NLABS with some supporting work done at Purdue University, School of Pharmacy and Pharmacal Sciences, Lafayette, Inliana (1).

Waterless hand cleaners are currently covered by Federal Specification P-H-31a, dated 21 February 1966. There is no Army interest in waterless hand cleaners except for those products covered by that Federal Specification. OCD has been purchasing hand cleaners in accordance with Type II, Class 2 of the specification, but with the addition of 0.2% hexachlorophene. This product in cream form is bacteriostatic and is formulated to remove greasy soils. The specification requires that it be stable when exposed to both 122°F. and 32°F. for 16 hours. These temperatures do not encompass the range of storage temperatures found in unheated shelters in the continental United States. NLABS Earth Sciences Laboratory advises that a temperature of -40°F. can be expected in unheated storage areas in the continental United States. The hand cleaner purchased under this specification separated during storage and the resultant liquid portion leaked at the crimped seam of the metal containers. The separation was evidently caused by the "break" of the emulsion when exposed to temperatures below 32°F. The leakage of the liquid was caused by the action of the solvent on the can seam-sealing compound.

2. Scope of the Study

The NLABS study included the following:

- a. Evaluate all feasible products and methods for the removal of hand soil, including paper cleansing towels and resin-base hand cleaners.
- b. Determine the low-temperature storage stability of commercial and laboratory-prepared waterless hand cleaners and compare the effect of the rapid freeze-thaw cycle as a substitute test method for the presently specified 16-hour exposure test.
- c. Initiate a study to develop a hand cleaner that will be stable and resistant to a freeze-thaw cycle.
- d. Investigate the inclusion of paper cleansing towels in the sanitation kit for cleaning and drying the hands, required if the current type of cleaner is continued in use.

- e. Investigate the relationships between the bactericidal effects of hexachlo.ophene, and the pH and emulsifier of the cleaner.
- f. Develop and test a suitable leak-proof packaging method for the hand cleaner recommended for OCD use.
- g. Prepare specifications for OCD procurement purposes covering the hand cleaner and packaging.

3. Laboratory Tests

Waterless hand cleaners were developed to remove grease and road dirt in the early days of motoring when the motorist had to make his own repairs. Present-day waterless hand cleaners are formulated for industrial use for the most part, and are not subjected to temperature extremes during storage. Most commercial cleaners contain organic soivents, surfactants, water, emulsifiers, emollients, perfumes, and sometimes fungicides and germicides.

Although there are numerous literature references on waterless hand cleaners, little information was found in these publications concerning stability at temperature extremes, particularly at low temperatures.

Drs. Donald J. Birmingham and Vernon B. Perone (20) of the U.S. Public Health Service evaluated 15 industrial hand cleaners for cutaneous irritation and conducted a study on the physiological factors associated with their usage for Wright Air Development Center, Dayton, Ohio. Laboratory tests covered such factors as free alkalinity or acidity, stability, relative cleansing efficiency, solvent content, residual effects on metals, defatting capacity, effects of hand cleaners having different pH values on the skin and eye, and toxicity. Tests were conducted on 500 volunteers over a peri of three months, during which time microscopic examinations of the hands were made. Stability tests were performed at 105°F. 70-80°F. and 20°F. Cleaning efficiency tests were done on polyethylene film, and on a 25 cm² area on the back of the hand. Five grams of cleaner were used, and the time for removal was recorded, using 2 minutes as the maximum allowable time. The test results showed that the skin was more difficult to clean than the polyethylene surface. This indicates that there is no suitable substitute for the practical test.

4. Test Methods to Determine the Cleaning Properties, Freeze-Thaw and Heat Stability of Waterless Hand Cleaners

A review of existing specifications and literature on waterless hand c eaners revealed that new requirements and test methods must be established to determine the cleaning properties, freeze-thaw stability and heat stability of waterless hand cleaners. The results of the NLABS study are included in this report.

a. Hand Cleaner Performance Tests

(1) Selection of the Soil

Available literature on the soils used for the evaluation of hard cleaners was reviewed and the results are discussed below.

Floor varnish, glue, used axle grease, India ink, mimeograph type ink, used crankcase oil (20W), 1% aqueous solution of gentian violet, flat coat wall paint, roofing tar, and household cement were used in evaluating the cleaning efficiency of various commercial products (20). These soils could be used for comparing the soil removal properties of the proposed product; however, because of the extensive amount of work involved, not all of these soils could be considered in this study.

It was determined that the dirt recovered from the bag of a household vacuum cleaner may resemble the soil(19) that accumulates in a fallout shelter. Here again, the problem arises of obtaining a uniform soil and duplicating results.

An asphalt emulsion (Korite L) has been used by some investigators as a soiling material. This material has the advantage of uniformity and could be easily duplicated; however, the exact concentration to be used could not be established.

A soiling mixture composed of 36.0 grams of air float grade charcoal mixed in 64 grams of Liquid Petrolatum (Heavy) U.S.P. is specified in evaluating a detergent-impregnated paper towel (21). This soiling mixture has certain advantages because it includes three difficult-to-remove products, such as a water insoluble material, an oil, and a coloring material.

The soiling material, specified in the Federal Specification for Waterless Hand Cleaners (22) for the past 11 years, has the following composition:

1 quart SAE #30 lubricating oil

1/2-pound lime grease

4 ounces carbon lamp black

6 ounces charcoal black

This soil has the advantage of being reproducible and has a satisfactory history of use in testing for soil removal. It was decided to use this soiling mixture as the criterion for determining the cleaning ability of the waterless hand cleaners.

(2) Hand Cleaner Test Procedure

A decision was made to use one hand-cleaning test procedure. Therefore, all of the waterless hand cleaners were tested for soil removal as follows:

Step 1: Both hands were washed with soap and water, and then dried. A waiting period of 15 minutes was then observed.

- Step 2: About 0.1 g. of the prepared soil was applied to the back of the left hand and knuckles with the right forefinger. The soil was rubbed into the skin lengthwise, crosswise, and in a circular motion for one minute.
- Step 3: The excess soil was removed with a paper towel conforming to Federal Specification UU-T-591, Federal Stock F. 8540-262-7178.
- Step 4: Then 1.0 g. of the cleaner under test was rubbed into the soiled skin area for 1 minute. The excess cleaner and the soil were wiped from the hand with a paper towel.
- Step 5: The operation described in Step 4 was repeated and the treated hand was compared with the unsoiled right hand. The removal was rated as excellent, good, fair, or poor as follows:
 - Excellent Soil was completely removed with no trace of skin discoloration.
 - Good Substantially all of the soil was removed with only a trace remaining in the creases of the knuckles.
 - Fair Soil remained in pores and knuckle creases.
 - <u>Poor</u> Soil remained in pores, knuckle creases, and on skin surface.

b. Freeze-Thaw Stability Test

The stability of the waterless hand cleaner to a freeze-thaw exposure was determined as follows:

A 25-gram sample of the waterless hand cleaner was placed into a one-ounce capped bottle. The bottle was exposed to a temperature of $-40^{\circ}F$. or $-26^{\circ}F$. for 18 hours and then kept at room temperature until thawed. The sample was subjected to this freeze-thaw cycle five times, or stopped sooner if separation occurred.

c. Heat Stability Test

The stability of the waterless hand cleaner to an elevated temperature was determined as follows:

A 25-gram sample was placed into a one-ounce capped bottle, exposed to a temperature of 155 to 160° F. for 4 hours and then cooled to room temperature. The sample was exposed to the heat cycle test five times. The test was stopped after 5 cycles or sooner if separation occurred.

Samples that with stood the freeze-thaw test were also subjected to the heat stability test.

5. Evaluation of Specification and Commercial Hand Cleaners.

Twenty-eight specification and commercial waterless hand cleaners were subjected to as many as five freeze-thaw tests, five heat stability tests and a soil removal test. The results are shown in Table I.

PERFORMANCE OF CURRENT SPECIFICATION-TYPE AND COMMERCIAL WATERLESS
HAND CLEANERS

41 Separation, 1	Sample No.*	Freeze-thaw Stability No. of Test Cycles	Heat Stability No. of Test Cycles	Soil Removal Rati.g
42 S1. Separation, 5 Separation, 2 43 Discolored, 5 Separation, 1 44 S1. Separation, 3 Separation, 2 45 No change, 5 Separation, 1 46 Discolored, 4 Discolored, 1 47 S1. Separation, 3 S1. Separation, 5 48 Discolored, 4 Discolored, 5 49 No change, 5 No change, 5 Fair 50 """ Separation, 5 51 """ No change, 5 Poor 52 """ No change, 5 Poor 52 """ "" Separation, 5 Poor 53 """ "" Separation, 5 Poor 54 """ "" Separation, 2 55 """ "" Separation, 2 56 """ "" Separation, 1 57 "" "" S1. Separation, 5 58 S1. Separation, 3 Separation, 1 59 No change, 5 No change, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 """ Note 1 62 No change, 5 Separation, 2 Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 """ "" " Fair	41	Separation, 1	••	
43 Discolored, 5 Separation, 1 44 S1. Separation, 3 Separation, 2 45 No change, 5 Separation, 1 46 Discolored, 4 Discolored, 1 47 S1. Separation, 3 S1. Separation, 5 48 No change, 5 No change, 5 Fair 50 """ Separation, 5 Separation, 2 Separation, 5 Separation, 6 Separation, 1 Separation, 2 Separation, 2 Separation, 1 Separation, 2 Separation, 2 Separation, 2 Separation, 2 Separation, 2 Separation, 2 Separation, 3 Separation, 3 Separation, 3 Separation, 2 Separation, 3 Separation, 5 Sepa	42	•	Separation, 2	
44 S1. Separation, 3 Separation, 2	43		-	
45 No change, 5 Separation, 1 46 Discolored, 4 Discolored, 1 47 Sl. Separation, 3 Sl. Separation, 5 48 No change, 5 No change, 5 Fair 50 """" Separation, 5 51 """" No change, 5 Poor 52 """" No change, 5 Poor 52 """" "" Separation, 5 Poor 53 """" "" Separation, 5 Poor 54 """" Separation, 2 Poor 55 """ "" Sl. Separation, 2 Poor 56 """" Sl. Separation, 1 Poor 57 """ Sl. Separation, 1 Poor 58 Sl. Separation, 3 Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 """ Note 1 62 No change, 5 Separation, 2 Poor 63 Separation, 1 Poor 64 No change, 5 Separation, 2 Poor 65 Separation, 1 Poor 66 No change, 5 Separation, 2 Poor 67 """ "" "Poor 68 Separation, 1 Poor 69 Separation, 1 Poor 60 No change, 5 Separation, 2 Poor 61 Separation, 1 Poor 62 No change, 5 Separation, 2 Poor 63 Separation, 1 Poor 65 Separation, 1 Poor 66 No change, 5 Separation, 5 Fair	44			€ 2
46 Discolored, 4 Discolored, 1 47 Sl. Separation, 3 Sl. Separation, 5 48 Discolored, 4 Discolored, 5 49 No change, 5 No change, 5 Fair 50 """ " Separation, 5 51 """ " No change, 5 Poor 52 """ " " No change, 5 Poor 53 """ " " " Excellent 54 """ " Separation, 2 56 """ " Separation, 5 57 "" " " Sl. Separation, 5 58 Sl. Separation, 3 Separation, 5 59 No change, 5 Sl. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 Separation, 1 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 Separation, 2 Poor 67 " " " " Poor 68 Separation, 1 69 No change, 5 Separation, 2 Poor 69 Separation, 1 60 No change, 5 Separation, 2 Poor 60 Separation, 1 61 No change, 5 Separation, 2 Poor 62 Separation, 1 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair	45		-	
S1. Separation, 3	46			
No change, 5	47		S1. Separation, 5	
Separation, 5 1	43	Discolored, 4	Discolored, 5	
51	49	No change, 5	No change, 5	Fair
52 " " " " " " " " " " Excellent 53 " " " " " " " " " " Fair 54 " " " " " Separation, 2 55 " " " " " " 4 57 " " " " " Sl. Separation, 5 58 Sl. Separation, 3 Separation, 1 59 No change, 5 Sl. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " " " " " " " " " " " " "	50	0 0 0 0	Separation, 5	
52 " " " " " Excellent 53 " " " " " " " " " Fair 54 " " " " " Separation, 2 55 " " " " " Sl. Separation, 5 57 " " " " Sl. Separation, 1 58 Sl. Separation, 3 Separation, 1 59 No change, 5 Sl. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " " " " " " " " " " " " "	51	11 11 11 11	No change, 5	Poor
54 " " " " Separation, 2 55 " " " " Sl. Separation, 5 57 " " " " Sl. Separation, 5 58 Sl. Separation, 3 Separation, 1 59 No change, 5 Sl. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	52			Note 1
55 " " " Separation, 2 56 " " " " Sl. Separation, 5 57 " " " " Sl. Separation, 5 58 Sl. Separation, 3 Separation, 1 59 No change, 5 Sl. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	53	11 11	11 11 11	Excellent
56	54	11 11	11 11 11	Fair
57 " " " " S1. Separation, 5 58 S1. Separation, 3 Separation, 1 59 No change, 5 S1. Separation, 5 Note 1 60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	55	11 11 11	Separation, 2	
58	56	11 11 15	11 11 4	
59 No change, 5 S1. Separation, 5 Note 1 60 No change, 5 Excellent 61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " " " " " " " "	57	11 11 11	Sl. Separation, 5	
60 No change, 5 No change, 5 Excellent 61 Discolored, 4 " " " Note 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	58	Sl. Separation, 3	Separation, 1	
61 Discolored, 4 " " " Note 1 62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	59	No change, 5	Sl. Separation, 5	Note 1
62 No change, 5 " " " Poor 63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	60	No change, 5	No change, 5	Excellent
63 Separation, 1 64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " " "	61	Discolored, 4	11 11 11	Note 1
64 No change, 5 Separation, 2 Poor 65 Separation, 1 66 No change, 5 No change, 5 Fair 67 " " " " " " "	62	No change, 5	11 11 11	Poor
65 Separation, 1 66 No change, 5 No change, 5 Fair 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	63	Separation, 1		
66 No change, 5 No change, 5 Fair 67 " " " " " " " "	64	No change, 5	Separation, 2	Poor
67 " " " " " " " " " " " " " " " " " " "	65	Separation, 1		
67 " " " " " " " " " " " " " " " " " " "	66	No change, 5	No change, 5	Fair
68 Separation, 1	67			11
	68	Separation, 1		

^{*} Identification Code for the Waterless Hand Cleaners is in Appendix A.

Note 1: Separation occurred on standing at room temperature, after completion of 5 freeze-thaw and 5 heat stability cycles.

Samples No. 53 and No. 60 were the only cleaners that did not separate after being subjected to both a freeze-thaw stability test and a heat stability test. They also exhibited excellent soil removal properties. Eighteen samples were resistant to the freeze-thaw test, but only 12 were resistant to the subsequent heat stability test.

The pH or hydrogen-ion concentration of the cleaners was determined. Most authorities (20, 23, 24) agree that the pH of skin is 4.0 to 6.5 and the pH of skin preparations should be within this pH range. A pH of 5.4 has been found to give the optimum germicidal action when an anionic surfactant and hexachlorophene are incorporated in a cleaner. Germicidal activity decreases with an increase in pH, and waterless hand cleaners containing hexachlorophene with either a nonionic or cationic surfactant should have less bacterial action than a product containing hexachlorophene and an anionic surfactant.

The pH of the 28 commercial waterless hand cleaners was determined on the undiluted cleaner, both electrometrically and with paper indicators. The names of the emollient and the germicide indicated on the label of these cleaners are listed in Table II.

TABLE II

LABEL INGREDIENT DATA AND DH VALUES OF COMMERCIAL WATERLESS HAND CLEANERS

* Label Ingredient Data			pH Value of Clea	ner
Sample No.	Germicide Present	Emollient Present	Glass Electrode	Indicator Pap
41	Hexachlorophene	Lanolin	7.6	7
42	11 - 11	11	8.4	7
43	11 11	*1	8.6	7
44	11 11	11	7.9	7
45	No information	No information	8.2	9
46	Hexachlorophene	Lanolin	8.6	8
47	No information	11	9.3	8
48	Hexachlorophene	11	8.4	8
49	11	11	7.7	8
5 0	No information	No information	8.2	7
51	11 11	11 11	8.0	8
5 2	11 11	11 11	8.4	8
53	11 11	11 11	7.8	7
54	Hexachlorophene	11 11	8.1	7
55	Bithinol	11 11	7.3	6
56	11	11 11	7.4	7
57	1+	11 11	7.3	7
58	3,4,4 -			
	Trichlorocarbinilide	11 11	7.6	7
59	Bithinol	11 11	7.6	7
60	No information	11 11	7.4	7
61	11 11	11 11	9.0	8
62	## ##	11 11	6.2	5
63	Hexachlorophene	Lanolin	7.9	7
64	11 11	11	5.6	5
65	II II	No information	7.2	7
66	11 11	Lanolin	4.2	5
67	11 11	.9	3.1	4
68	11 11	No information	9.3	9

^{*} Identification Code for the Waterless Hand Cleaner is in Appendix A.

The average pH of all cleaners is 7.6, and average pH of those cleaners containing hexachlorophene is 7.3. Eighty-six percent of the cleaners have a pH above 7.0; however, the pH of only 3 cleaners is within 4.0 to 6.5 range.

b. Commercial Waterless Hand Cleaner (C-7)

(20)

A cream identified as C-7 (69) in the U.S. Public Health Service report proved to be outstanding. This cream includes petroleum oil and surface active agents. This product is supplied in one pint, screw-top, wide-mouth, metal cans. The manufacturer advertises that the cream contains hexachlorophene, lanolin, and blended emollients. The results of an evaluation of this product at NLABS are tabulated in Table III.

TABLE III

LABORATORY EVALUATION OF AN OUTSTANDING COMMERCIAL CLEANER C-7

Test	Result		
Freeze-thaw (-40°F. to 76°F.)	No change		
Heat stability (155°F.)	No change		
Shelf stability	No change in 4 months		
Color and form	White cream		
Emulsion type	Oil in water		
pH	6.0		
Soil removal	Good - Excellent		
Odor	Slightly perfumed		
Loss at 105 ⁰ C.	56%		

c. <u>Commercial Waterless Hand Cleaner Packaged in a Pressurized Container</u> (Sample 70)

This cream is packaged in a pressurized cylindrical metal container two inches in diameter by 5-1/4 inches high. The gross weight is 5.8 ounces and the contents weigh 4 ounces. This commercial cleaner, identified as Sample 70, is advertised for the removal of grease, tar, paint, ink, carbon, shoe polish and hard-to-remove soils, and may be used with or without water.

The soil removal rating of this product was excellent. The cream "broke" into a solvent and another liquid phase in approximately 0.6 minute during the soil removal test. Delivery of the cream from the spout was sluggish at temperatures below 70°F. The container and contents will not withstand freezing or heating. The retail cost of this product is \$0.59 per container, or \$2.36 per pound.

d. Commercial Resin-Based Waterless Hand Cleaner (V-T)

This proprietary product was advertised as a waterless-towel-less hand cleaner. A small quantity of the product is applied to the hands and spread by rubbing; after a few seconds, the product begins to dry and "pill." With additional rubbing, the soft resin residue with dirt embedded is rubbed off. When frozen and then allowed to thaw, the product formed a thin gel. The hand-cleaning action was rated good to fair. The air-dried preparation sometimes adhered tenaciously to hair and its removal caused some discomfort.

e. Towel, Paper Cleansing, Wet

Another phase of the work included the evaluation of wet paper cleansing towels. These towels, covered by Military Specification MIL-T-43007(QMC), are for removing ordinary or fairly-difficult-to remove soils from the hands, face and body without using soap, water or another towel. These towels were not effective in removing heavy soil. Freezing and then thawing of the packaged towels did not adversely affect their performance. The towels cost \$0.0165 each, are stable to freeze-thaw, occupy small cubage, and are self-sufficient to clean and dry the hands.

6. Experimental Formulations

a. Freeze-Thaw Resistant Cleaners

M.N. Cruse and D.L. Miller described four waterless hand cleaners that have been subjected to 10 freeze-thaw cycles and to a temperature of 130°F. for 200 hours without any separation (25). Three of these cleaners contain deodorized kero-ene; the fourth contains light mineral oil. The latter composition was of interest because it overcomes the dermatologist's objection to the use of kerosene in hand cleaners. The compositions of these waterless hand cleaners are described in Table IV.

COMPOSITION OF FOUR WATERLESS HAND CLEANERS
ALLEDGED TO HAVE STABILITY TO TEMPERATURE EXTREMES

Ingredients	CM#1 Percent	CM#2 Percent	CM#3 Percent	CM#4 Percent
Deodorized kerosene	39.2	39.1	37.1	
Light mineral oil				32.2
Dipropylene glycol methyl ether			2.0	2.1
Tall oil fatty acid	4.1	7.5	7.5	10.7
Stearic acid	3.5			
Mixed isopropanolamine		3.7	3.7	3.8
Nonylphenol ethylene oxide adduct (1) (Surfactant)	2.0	2.0	2.0	4.3 (2)
Monoethanolamine	0.8			••
Triethanolamine	2.6			
Propylene glycol	2.5	2.5	2.5	4.3
Glycerine	1.0	1.0	1.0	
Lanolin	0.5	0.50	0.5	
Distilled water	43.8	43.7	43.7	42.6
t ot	al 100.0	$1\overline{00.0}$	100.0	$1\overline{00.0}$

- (1) Dowfax 9NO
- (2) Dowfax 9N10

(1) Preparation of CM#1

The kerosene, tall oil fatty acid, and stearic acid were mixed together and heated to 160°F. to form the oil phase. The monoethanolamine, triethanolamine, surfactant, propylene glycol, glycerine, and melted lanolin were dispersed in the distilled water. The water phase was added to the oil phase while stirring.

(2) Preparation of CM#2

Kerosene, tall oil fatty acid, and melted lanolin were mixed together to form the oil phase. The isopropanolamine, surfactant, propylene glycol, and glycerine were dissolved in distilled water to form the water phase. This latter mixture was heated to 120° F. to form a solution. The water phase was added to the oil phase while stirring.

(3) Preparation of CM#3

This emulsion was produced in the same manner as that used to prepare CM#2.

(4) Preparation of CM#4

The mineral oil, glycol ether, and tall oil were mixed together. The isopropanolamine, surfactant, and propylene glycol were dissolved in water heated to $112^{\rm o}$ F. The water phase was added to the oil phase while stirring.

(5) Physical Properties and Performance

A laboratory evaluation of these four products produced the following results:

Physical Property	CM#1	<u>CM#2</u>	<u>CM#3</u>	<u>CM#4</u>
Color	white	light cream	light cream	white
Form	thick cream	thin cream	lotion	lotion
Emulsion Type Freeze-Thaw (-26°F-room temp)	Oil/water stable to 5 cycles	Oil/water several oil drops, separated	separate	d several oil drops
		after 5 cycles, darkened slightly		d cycles, separated after 6 months
Soil Removal	good	excellent	fair	excellent

b. <u>Industry-Recommended Cleaners</u>

In a letter from a surfactant manufacturer, two paste products containing an isoparaffinic solvent were recommended as effective hand cleaners. These cleaners were compounded at NLABS and identified as A-1 and A-2. A second manufacturer (27) recommended a formulation based on the same isoparaffinic solvent. This formulation was also made at NLABS and was identified as H-1. Compositions of the three products are listed in Table V.

(1) Preparation and Evaluation of A-1

The lanolin, Span 80, Tween 60, cetyl alcohol, and hexachlorophene were dissolved in the Isopar M heated to $158^{\circ}\mathrm{F}$. The sorbitol was mixed with distilled water and heated to $161^{\circ}\mathrm{F}$. The water phase was added slowly to the oil phase while agitating. The resultant white emulsion was fluid while warm but thickened after cooling.

After 5 freeze-thaw cycles ($-26^{\circ}F$ to room temperature), one oil droplet separated from a 25-gram test sample. Soil removal rating was good. The emulsion separated during the heat stability test. The sample stored at room temperature for approximately 8 months developed mildew.

(2) Preparation and Evaluation of A-2

The lanolin, Arlacel 60, Tween 60, cetyl alcohol, G-11, and paraffin wax were dissolved in Isopar M heated to $158^{\circ}F$. The glycerine was dissolved in distilled water and heated to $161^{\circ}F$.

COMPOSITION OF INDUSTRY-RECOMMENDED CLEANERS
CONTAINING ISOPARAFFINIC SOLVENT
(Recommended by Surfactant Manufacturers)

Ingredients		A-1 Percent	A-2 Percent	H-1 Percent
Isoparaffinic hydrocarbon (Isopar M)		40.0	30.0	33.3
Lanolin		1.0	1.0	3.3
Paraffin wax			2.0	
Oleic acid			**	10.3
Triethanolamine				2.6
Monoethanolamine			••	0.9
Sorbitan monooleate (Span 80)		1.6		
Sorbitan monostearate (Arlacel 60)			1.0	
Polyoxyethylene sorbitan monostearate (Tween 60)		6.4	4.0	••
Alkyl phenyl polyethylene glycol (Tergitol NPX)				4.1
Cetyl alcohol		7.0	3.0	
Hexachlorophene (G-11)		0.2	0.2	0.2
Sorbitol (Sorbo)		5.0		•-
Propylene g. 1				4.1
Glycerine			5.0	
Distilled water		38.0	53.8	41.2
	total	100.0	100.0	100.0

The water phase was added to the oil phase while stirring. The resultant white emulsion remained fluid. This lotion was unaffected after 5 freeze-thaw cycles (-26°F. to room temperature), but was rated poor when tested for soil removal.

(3) Preparation and Evaluation of H-1

The oil phase was prepared by dissolving oleic acid, triethanolamine, monoethanolamine, lanolin, and hexachlorophene in Isopar M. Propylene glycol and Tergitol NPX were dissolved in distilled water to form the water phase. The water phase was added to the oil phase while stirring. The finished product was a light tan, thick cream. After 4 freeze-thaw cycles (-26°F. to room temperature), the emulsion "broke" and formed two layers. The product was rated excellent when tested for soil removal.

c. University and Industry-Recommended Cleaners

Fersonnel at Purdue University recommended a cleaner similar to that covered by U.S. Patent 2,567,999. Two formulations covered by this patent were made at NLABS. These products are identified as P-1 and P-1A (Table VI) for composition. A technical bulletin (28) on surface active agents includes a typical formula for waterless hand cleaner. This emulsion was made and evaluated at NLABS and was identified as B-1 (see Table VI for composition).

TABLE VI

COMPOSITION OF UNIVERSITY AND INDUSTRY-RECOMMENDED CLEANERS

CONTAINING PETROLEUM NAPHTHA

		P-1	P-1A	B-1
Ingredients		Percent	Percent	Percent
Oleic acid		13.8	12.4	9.1
NH ₄ OH (10%)		6.0	5.3	
NaOH (20%)		3.4	3.1	
Petroleum naphtha		75.0	68.5	
Hexachlorophene (G-11)		0.2	0.2	
Distilled water			9.3	43.2
Glycerine		1.5	1.2	
Mineral oil				35.0
Ethylene oxide adduct of				
castor oil (Surfactol 365)				5.2
Propylene glycol				4.3
Triethanolamine				2.3
Monoethanolamine				0.9
	total	99.0	$1\overline{00.0}$	100.0

(1) Method of Preparation

Sample P-1

The hexachlorophene was dissolved in oleic acid and naphtha was then added. In a separate beaker, NH_4OH , NaOH, and glycerine were mixed and added to the naphtha mix while stirring.

Sample P-1A

Naphtha, oleic acid, and NH₄OH were mixed together. NaOH, distilled water, glycerine, and hexachlorophene were added while stirring.

Sample B-1

Mineral oil, oleic acid, Surfactol 365, and propylene glycol were mixed together. Triethanolamine and monoethanolamine were dissolved in water and added to the former mixture while stirring.

(2) Physical Properties and Performance

Physical Properties	<u>P-1</u>	<u>P-1A</u>	<u>B-1</u>
Color and form Odor Emulsion type	Amber jell Heavy Aromatic Oil/Water	Amber, liquid Aromatic Oil/Water	Light tan lotion Very little Oil/Water
Performance			and appropriate the second sec
Freeze-thaw (-30°F to 76°F)	-	- :	Slight separation
Room storage	Slight separation	Slight separation	Separace
Heat stability (155°F)	No change	-	Phase separation
Soil removal	Good	Fair	-

d. Industry-Compounded Waterless Hand Cleaners (x127 and x476)

Two additional samples were furnished by another chemical company. These products were identified as X127 and X476. The composition of these products is listed in Table VII.

TABLE VII

COMPOSITION OF INDUSTRY-COMPOUNDED CLEANERS

Ingredients

Portion A		X127 Percent	X476 Percent
Hexachlorophene (G-11)		0.25	0.25
Isopropyl ester of myristic and palmitic acids (Deltyl Extra) Propylene glycol Triethanolamine		3.00	3.00 3.00
Portion B			
Mineral oil Deodorized kerosene Oleic acid Perfume oil Distilled water Tetradosium salt of ethylene diaminetetraacetic acid (Versene 100)		25.00 33.00 8.00 .30	39.55 0.10
Portion C			
Triethanolamine Glycerine Distilled water Carboxyvinyl polymer (1% Carbonal 941 neutralized') to 5.2 pH).		4.00 2.00 27.45	10.00
Portion D			
Deodorized kerosene Oleic acid Mineral oil Sulfosuccinic esters (Mona Pearl)			25.00 6.00 10.00 3.00
Portion E			
Perfume oil	tota1	100.0	$\frac{.10}{100.00}$

Methods of preparation furnished by the manufacturer were as follows:

Sample X127

Portion A was weighed into a large container and heated to dissolve the hexachlorophene. When this solution was clear, the ingredients or Portion B were added.

In a separate container, Portion C was then added slowly to the mixture of Portions A and B while the mix was stirred rapidly. Agitation was continued until a smooth emulsion was obtained.

Sample X476

The hexachlorophene was dissolved in heated propylene glycol and triethanolamine. Portions B and C were added and the mix heated to $167^{\circ}F$. The ingredients of Portion D were placed into a large container and heated to $167^{\circ}F$. The mix of A,B, and C was added to Portion D and the emulsion stirred and cooled to $113^{\circ}F$. Portion E was then added.

(2) Physical Properties and Performance

Physical Properties	Sample X127	Sample X476
Color and form Odor Type emulsion	Tan cream Mild Oil/Water	White lotion Mild Oil/Water
Performance		
Freeze-thaw (-25°F. to 72°F.)	No change - Did not freeze solid.	Separation on standing after
Heat stability (155°F.) Soil removal	Slight separation Excellent	test. Excellent

e. Purdue University Kerosene Waterless Hand Cleaners

Purdue University made a series of experimental emulsion creams with a kerosene base; the compositions of these cleaners are listed in Table VIII.

TABLE VIII

COMPOSITION OF KEROSENE SOLVENT CLEANERS MADE AT PURDUE UNIVERSITY

(Ingredients in gm or cc)

Ingredients	1	2	3	4	5	6	7	8
Kerosene	65	40	45	50	50	55	60	60
Polyoxyethylene sorbitan trioleate	5	5	5		5	5	5	5
(Tween 85)								
Polyoxethylene sorbitan monooleate	15	15	15		15	15	15	15
(Tween 80)								
Distilled water	15	40	35	27	30	25	20	28
Polyethylene glycol 400				12				
Stearic acid				4				
Triethanolamine				6.5	5			
Methocel (4000 cps.)								2
Ingredients	9	10	11	12	13	14	15	16
Kerosene	60	60	60	60	60	60	60	60
Polyoxyethy ne sorbitan trioleate	5	5	5	5	5	5	5	5
(Tween 85)								
Polyoxyethylene sorbitan monooleate	15	15	15	15	15	15	15	15
(Tween 80)								
Distilled water	30	20	23	19	18	18.5	19.75	
Methocel (4000 cps.)	0.9	5	0.5	5				
Hexachlorophene	3.1	l2 3.	L5 1	0.5	1.0	0.5	9.5	0.5
Lanolin	1				\$.5	0.5		
Pumice	_				V., J	3.5	0.25	

(1) Test Results

One specimen of each sample was held in a constant temperature oven at $122^{\circ}F$. for three weeks. Another specimen was held for three weeks in the freezer compartment $(14^{\circ}F)$ of a refrigerator. Of those products prepared and tested, the product that showed the best performance was Formula No. 14.

(2) Physical Properties and Performance

The physical properties and the performance of Formula No. 14 when tested at NLABS were as follows:

Physical Properties

Color and form

- Grayish white stiff cream

Emulsion type

- Oil/Water

Performance

Freeze-thaw (-30 $^{\circ}$ F. to 75 $^{\circ}$ F.) - 0.6cc liquid separated from 25 gram

samples.

Heat stability (155°F.)

- Slight darkening

Soil removal

- Good

Shelf stability

- Dark on top after 4 months

f. Waterless Hand Cleaners with Varying Water Content

A series of creams was prepared, each with a different quantity of water, to determine the stability and cleaning properties of the end item. The compositions of these creams are listed in Table IX.

TABLE IX

COMPOSITION OF CLEANERS WITH DIFFERENT WATER CONTENT

Ingredients	M-1 (grams)	M-4 (grams)	M-5 (grams)	M-2 (grams)	M-3 (8%Md)
Phase A					
Deodorized kerosene	25	29	31	38	43
Light mineral oil	10	14	16	25	28
Tall oil fatty acid	8	8	8	8	6
Stearic acid					2
Dipropylene glycol methyl ether	3	3	3	3	2
Lanolin	1	1	1	1	1
Phase B					
Distilled water	44	40	36	16	12
Mixed isopropanolamine	2	2	2	2	3
Glycerine	3	3	3	3	3

Physical Properties

(-26°F to 78°F) Soil removal

The lanolin and stearic acid were melted prior to addition to the other ingredients of Phase A. The ingredients of Phase B were added slowly to Phase A, while the mixture was being stirred.

(2) Physical Properties and Performance

M-1

Emulsion type Color and form Odor	Oil/Water Light tan lotion Ether	Oil/Water White lotion	Oii/Water Light tan lotion Ether	Oil/Water Yellow liquid Sl.Ether	Oil/Water Yellow liquid Very Slight
Performance Freeze-thaw	separated	separate	d separate	d separate	Ether ed separated

M-4

M-5

excellent

M-2

excellent

M-3

excellent

g. Waterless Hand Cleaners with Different Hydrocarbon Solvents

excellent

A series of creams was prepared, each with a different hydrocarbon solvent, to determine physical properties and performance, especially the difference in odor; they are shown in Table X.

excellent

TABLE X

COMPOSITION OF CLEANERS WITH DIFFERENT HYDROCARBON SOLVENTS

Ingredients	M-5 Percent	M-5B Percent	M-5C Percent
Phase A			
Isoparaffinic hydrocarbon (Isopar M) Isoparaffinic hydrocarbon	31		
(Isopar H)		31	
Petroleum solvent (Marcol 52)			31
Mineral Oil	16	16	16
Tall Oil Fatty Acid	8	8	8
Lanolin	1	1	1
Phase B			
Glycerine	3	3	3
Diprorylene glycol methyl ether	3	3	3
Mixed isopropanolamine	2	2	2
Distilled water	36	36	36

Lanolin was melted before being added to the other ingredients in Phase A. The ingredients in Phase B were then slowly added to the ingredients in Phase A while the mixture was stirred.

(2) Physical Properties and Performance

Physical Properties	<u>M-5A</u>	<u>M-5B</u>	<u>M-5c</u>	
Color and form	Light tan	Light tan	Light tan	
Emulsion type Odor	Oil/Water Mild	Oil/Water Very little	Oil/Water Little	
Performance				
Freeze-thaw (-30°F to 76°F)	Separated	Separated	Separated	
Shelf stability	Separated	Separated	Separated	

h. Waterless Hand Cleaners with Added Perfumes

A series of emulsions was prepared and perfume oils were added to mask any kerosene odor. (Table XI)

TABLE XI

COMPOSITION OF CLEANERS WITH PERFUME OILS ADDED

Identification	<u>M5-1</u> (grams)	<u>M5-2</u> (grams)	<u>M5-3</u> (grams)	M5-4 (grams)	<u>M5-5</u> (grams)
Phase A	(8)	(8	/8/	(8	(8)
Deodorized kerosene Light mineral oil Tall oil fatty acid Lanolin	31 16 3 1	31 16 0 1	31 16 7	31 16 8 1	31 16 3 1
Phase B					
Mixed isopropanolamine Glycerine Distilled water Dipropylene glycol methyl ether Lilac C710 Tutti Frutti 1346 Wetwood pine C 717	2 3 36 3 3.6	2 3 36 3	2 3 36 3	2 3 36 3	2 3 36 3
Appleblossom C695 Mint C 712			2.0	1.0	1.0

Melted lanolin was added to the other ingredients in Phase A. The ingredients in Phase B were slowly added to the Phase A ingredients while the mixture was stirred. The large batch was divided into six parts and a perfume oil was blended into each of five portions.

(2) Comments

Comments on the odor were as follows:

M5-1 - Emulsion odor pleasant. When applied to the skin, the scent is rather strong but leaves a pleasant odor when wiped off with a paper towel.

M5-2 - Emulsion tinted to a light brown; odor is too sweet and fruity.

M5-3 - Emulsion has an agreeable odor. Product leaves a faint, pleasant odor on the skin.

M5-4 - Emulsion has delicate odor. Leaves a faint, not unpleasant odor on the skin.

M5-5 - Spicy, disinfectant odor.

i. Purdue-prepared Emulsions with Kerosene and Various Emulsifiers

At Purdue University, three series of semi-solid emulsions were made with kerosene and emulsifiers. The composition, form, and stability of the emulsions are listed in Tables XII-A, B and C.

TABLE XII-A

COMPOSITION OF SIMPLE EMULSIONS MADE AT PURDUE UNIVERSITY

(Ingredients in Grams or cc)

Ingredients	33	34	35	36	37	38
Kerosene	60	60	60	6 0	60	60
Polyoxyethylene sorbitan	-	-	5	10	15	20
monolaurate (Tween 20)	r	5				
Polyoxyethylene sorbitan moncoleate (Tween 80)	5	5	•	-	-	-
Polyoxyethylene sorbitan	15	15	-	-	-	-
trioleate (Tween 85)	0.5	0.5	0.5	0.5	0.5	0.5
Hexachlorophene Lanolin	0.5	0.5	0.5	0.5	0.5	0.5
Distilled water	13.9	13.9	33.5	28.5	23.5	18.5
Stability to Temperature (14°F to 122°F)	b	а	С	С	С	С

Legend

a - Slight separation; b - Moderate separation; c - Severe separation.

TABLE XII-B

redients	39	40	41	42	43
osene	60	60	60	60	60
yoxyethylene sorbitan nolaurate (Tween 20)	5	10	15	20	•
yoxyethylene sorbitan nooleate (Tween 80)	-	•	•	-	5
yoxyethylene sorbitan ioleate (Tween 85)	•	•	•	•	15
achlorophene	0.5	0.5	0.5	0.5	0.5
olin	0.5	0.5	0.5	0.5	0.5
ic acid	5	10	15	20	•
tilled water hylcellulose	33.5	28.5	23.5	18.5	18.9 1
bility to Temperature (14°F. to 122°F.)) NS	NS	NS	NS	S
ioleate (Tween 85) achlorophene olin ic acid	0.5 5 33.5	0.5 10 28.5	0.5 15 23.5	0. 20 18.	5

Legend

NS - Not suitable for testing; S-Stable

TABLE XII-C

Ingredients	44	45	46	47	48	49	50
Kerosene	10.	10	10	10	10	10	10
Polyoxyethylene sorbitan monostearate (Tween 61)	2.5	2.5			2.5	2.5	2.5
Sorbitan monostearate (Span 60)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Paraffin, USP	22.5	5	10	15	20	25	30
Distilled water	75	75	75	75	75	75	75
Stability to Temperature (14°F. to 122°F.)	С	С	С	С	С	С	С

Legend

c - Severe separation

None of these compositions offered much promise due to poor cleaning action and instability.

j. Effect of Agitation on the Stability of M-5B During Preparation

Simple mixing equipment was used in the production of the emulsions. A colloid mill or emulsifier was ruled out in the interest of simplicity of manufacture and economy. A series of emulsions, however, was made using a Waring blendor as follows:

(1) Method of Preparation

An emulsion was produced according to formulation M-5B, as described earlier, except that a Waring Blendor was used to combine the ingredients. The emulsion was agitated one minute and then scraped from the sides of the container. This was repeated for 5 cycles, then a 100-gram sample was removed and labeled A. After 3 more cycles, a second sample, identified as B, was removed. A third sample, identified as C, was removed after 2 more cycles, and, finally, a sample identified as D was removed after an additional one-minute cycle.

(2) Physical Properties and Performance

Physical properties	All Samples
Color Odor Consistency	White opalescent Mild Jell-soft

<u>Performance</u>

Freeze-thaw (-26°F to 76°F)	Separated
Heat stability (155°F)	Separated

k. Purdue-Prepared Cleaners with Different Kerosene Contents

A series of experimental creams was made at Purdue University in which the percentage of kerosene was varied. None of these creams showed good stability. The compositions are shown in Table XIII.

TABLE XIII

COMPOSITION OF A SERIES OF CLEANERS WITH DIFFERENT AMOUNTS OF KEROSENE

(Ingredients in grams or cc)

Ingredients	111	112	113	114	115	116	117	118	119	120
Kerosene	60	50	_	30	20	_	_	5	10	15
	5	5	5	50	20	_	_	_	-	-
Polyoxyethylene sorbitan trioleate (Tween 85)				•	•	•	•	-	-	-
Polyoxyethylene sorbitan monooleate (Tween 80)	15	15	15	-	2	•	2	2	2	2
Sorbitan monostearate (Span 60)	-	-	•	2	2	2	2	2	2	2
Castile soap NF	•	-	-	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Hexachlorophene	0.5	0.5	-	•	-	-	-	-	-	-
Lanolin	0.5	0.5	-	-	-	-	-	-	-	-
Light liquid petrolatum	-	-	60	15	15	15	15	15	15	15
Glycerin USP	_	-	-	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Distilled water	18.9	_	20	35	35	35	35	35	35	35
Methocel (400 cps.)	10	-	•	•	•	•	•	-	-	-
Cilicone oil	6	-	-	-	-	-	_	-	-	-
Alcohol	6	-	-	-	-	-	-	-	_	•
25% Borax solution	•	18.5	•	-	-	-	-	-	-	-
To and if on to	121	122	123	124	125	126	127	128	129	130
Ingredients	121	122	123	124	_125	120	12/	128	129	130
Light liquid petrolatum	30	30	30	30	30	3 0	30	39	3 0	30
Kerosene	-	-	5	10	15	-	-	-	-	-
Triethanolamine	5	5	10	10	5	5	5	5	5	5
Oleic acid	10	15	20	20	10	11	12	13	14	10
Distilled water	45	45	45	45	45	رب	45	45	45	45
Starch paste (8g/50cc H ₂ 0)	10	10	5	5	10	10	10	10	10	10
			_	_						_ •

1. Purdue-Prepared Cleaners with Different Mineral Oil Contents

A series of creams, commonly identified as "cleansing" creams, was prepared at Purdue University using varying amounts of mineral oil (Table XIV). Cleansing properties and stability at 14°F. and 122°F. were determined. None of these products were outstanding and all were inferior to the commercial product, identified as Sample No. 69, which was used for comparison purposes.

TABLE XIV

COMPOSITION OF CLEANERS WITH DIFFERENT AMOUNTS OF MINERAL OIL

(Ingredients in grams or cc)

Ingredients	131	132	1.	33	134
Light liquid petrolatum	30	40	41)	40
Triethanolamine	5	4.4		4.4	4.4
Oleic acid	10	12	1:		12
Distilled water	45	50	40)	40
Starch clycerite NF	10	•	•		-
Polyoxyethylene sorbitan mono- laurate (Tween 20)	•	5	•		-
Propylene glycol	-	5	!	5	5
Sorbitan monolaurate (Span 20)	-	•	1	5	•
Sorbitan monooleate (Arlacel 80)	-	-	-		5
Anhydrous lanolin	5	-	:	3	3
Ingrediencs	135	136	137	138	139
Light liquid petrolatum	40	40	40	40	40
Oleic acid	12	12	12	12	12
Triethanolamine	4.4	4.4	4.4	4.4	4.4
Sorbitan monooleate (Arlacel 80)	7.5	7.5	8.5	9.5	10.5
Propylene glycol	5.0	5.0	5.0	5.0	5.0
Distilled water	40	40	40	40	40
Anhydrous lanolin	-	3	3	3	3

m. Effect of Different Amounts of Emulsifiers on Emulsion Stability

A series of creams was made to determine the effect of different amounts of a surface agent on the consistency and stability of the emulsion.

TABLE XV

COMPOSITION OF CLEANERS WITH DIFFERENT AMOUNTS OF SURFACTANTS

Ingredients	S-1	S-2	S-3	S-4	S-5
Phase A					
Isoparaffinic hydrocarbon (Isopar H)	30g.	30g.	30g.	30g.	30g.
Light mineral oil	15	15	15	15	15
Tall oil fatty acid	8	8	8	8	8
Lanolin	1	1	1	1	1
Glycerine	3	3	3	3	3
Dipropylene glycol methyl ether	3	3	3	3	3
Sorbitan monostearate (Span 60)	2	4	6	8	
Polyoxyethylene sorbitan mono- stearate (Tween 60)					2
Phase B					
Distilled water	36	36	36	36	36
Mixed isopropanolamine	2	2	2	2	2

The ingredients in phase A were heated to $168^{\circ}F$, then the well-section (phase B) was added slowly at $74^{\circ}F$. Phase A was stirred with a Dormey winds during emulsification.

(2) Physical Properties and Performance

Physical properties	<u>s-1</u>	<u>s-2</u>	<u>s-3</u>	<u>s-4</u>	<u>s-5</u>
Comparative consistency Color and form	Light White lotion	Light Light tan lotion	Light Light tan lotion	Heavy Off-white lotion	Medium Off-white locion
Performance					
Freeze-thaw (-30°F to 74°F) Shelf stability (2 mos)	No change ''	No change 11	No change	No change ''	
Heat stability (155°F)	Sep.	Sep.	Sep.	Sep.	

n. Purdue-Prepared Cleaners with Varying Amounts of Emulsifiers

A series of cleaners using an isoparaffinic hydrocarbon and mineral oil with different amounts of surfactants formulated by Purdue University are shown in Table XVI.

TABLE XVI

COMPOSITION OF CLEANERS MADE AT PURDUE UNIVERSITY
CONTAINING DIFFERENT AMOUNTS OF SURFACTANTS

Ingredients	140	141	142	143	144	145
Isoparaffinic hydrocarbon (IsoparH)	29	. 9	39	29	29	1
Light liquid petrolatum	1.	4.5	1	1.5	15	ž. *
Oleic acid	۳.	<u>-1</u>	Γ.	5	7	-
anolin	1	1	1	1	1	_
Slycerin	2.4	2.4	2.4	2.4	2.4	2 9
Sorbitan monopalmítate (Span 40)	2	3	4	5	6	-
Polyoxyethylene sorbitan monooleate (Tween 80)	3	2	2	2	2	ż
lexachlorophene	0.5	0.5	0 5	0.5	0.5	0.5
Distilled water	35	35	7.5	35	.45	N5
Castile soap	_	-	-	-	-	7 0
Sorbitan monostearate (Span 60)	~	-	-	-	•	2

Formula No. 145 was the most promising product developed by Purdue University. This cream was tested there and found satisfactory from the standpoint of soil removal, ease of application, ease of removal, stability at $14^{\circ}F$ and $122^{\circ}F$, non-irritation to the user, and bactericidal action. Samples of this cream were supplied to NLABS for evaluation. The results were as follows:

Color -	Tan
	Semi-fluid cream
	(-30° to 77°F) - One specimen separated badly, three triplicates also separated.
•	(-40°F to 78°F) - Three triplicate specimens separated on first cycle.
Heat stability (155°F) -	Slight darkening
Shelf stability -	Separated in original container after several months
Odor -	Mildly fatty
pH -	6
Soil removal -	Fair to poor

o. The Effect of Substitution of Stearic Acid for Tall Oil Fatty Acid in S-1 Composition

Cleaner composition S-1 was prepared by substituting stearic acid for the tall oil fatty acid and is shown in Table XVII.

TABLE XVII

COMPOSITION OF STEARIC ACID-ISOPROPANOLAMINE SOAP CLEANER

Phase A	Percent
Isoparaffinic hydrocarbon (Isopar H) Light mineral oil Stearic acid	30 15 8
Lanolin Glycerine Sorbitan monostearate (Span 60) Dipropylene glycol methyl ether	3 2 3
Phase B	
Water Mixed isopropanolamine	36 2

The ingredients in Phase A were heated to $180^{\circ}\mathrm{F}$ to obtain a solution. The ingredients in Phase B were slowly added to Phase A while the mixture was being stirred in a Dormey mixer. The resulting emulsion was then stirred for 15 minutes. The emulsion was curdy and it was reheated to $180^{\circ}\mathrm{F}$, stirred at speed 3 for 15 minutes, and then cooled to room temperature.

One half of this batch was labeled "S-1(M)" and the other half labeled "S-2(M)". The "S-2(M)" portion was processed through a laboratory hand-homogenizer and was tested and compared with sample S-1(M).

An attempt to disperse portion S-1(M) in a Waring Blendor and in an Eppenbach Homo-Mixer was unsuccessful because of the high viscosity of the cream.

Test Results	$\underline{S-1(\underline{M})}$	$\underline{S-2(\underline{M})}$
Color and form	Heavy white cream	Heavy white cream
Emulsion type	Oil/Water	Oil/Water
Heat stability (155°F) Freeze-thaw (-26°F to 74°F)	No change	No change
Freeze-thaw (-26°F to 74°F)	No change	No change
Odor	Ether	Ether
Residue on skin	Greasy	Greasy

p. Effect of an Anionic Surfactant on Viscosity and Residual Greasiness.

An anionic surfactant was added to the most promising composition to lower the viscosity and to reduce the residual greasiness. These products showed stability to temperature extremes equal to or better than any commercial products. In addition, these products showed good soil removal properties(Table XVIII).

TABLE XVIII

COMPOSITION OF CLEANER WITH ADDED ANIONIC SURFACTANT

Ingredients	<u>ST-3</u>
Phase A	Percent
Isoparaffinic hydrocarbon (Isopar H) Light mineral oil Lanolin Stearic acid Dipropylene glycol methyl ether Glycerine	29 15 1 3 3
Phase B	
Distilled water Mixed isopropanolamine Sodium tetradecyl sulphate (Tergitol Anionic)	36 4 1

The ingredients in Phase A were heated to 180°F. The ingredients in Phase B were added slowly while the cil mixture was stirred in the Dormey mixer. The white cream was mixed for 15 minutes to form a homogeneous emulsion.

(2) Physical Properties and Performance

Physical property

Color and form White cream Odor Ether-like Residue on skin Not greasy

Performance

Freeze-thaw (-30°F to 74°F) No change Heat stability (155°F) No change Shelf stability (2 months) No change

q. Color and Odor Improvement by the Addition of Titanium Dioxide, Polyvinylpynolidone and Perfume

Other modifications were made to improve the color stability and odor of the most promising cream. Dipropylene glycol methyl ether was eliminated from the product because of the report (29) that this solvent leaves a faint, persistent odor on the skin which was found objectionable by industrial workers in field tests (Table XIX).

TABLE XIX

COMPOSITIONS WITH THE ADDITION OF SMALL AMOUNTS OF PIGMENT, PROTECTIVE COLLOID,

AND PERFUME

Identification	ST-4	ST-4A	ST-4B	ST-4C	ST-4D	ST-4E
Phase A						
Is <mark>oparaffini</mark> c Hydrocarbon (Isopar I	1) 31	31	31	31	31	31
Light mineral oil	16	16	16	16	16	16
anolin	1	1	1	1	1	1
Slycerine	3	3	3	3	3	3
Stearic acid	G	3	3	3	8	8
Phase B						
istilled water	36	36	36	36	36	36
lixed isopropanolamine	4	4	4	4	4	4
odium tetradecyl sulphate	1	1	1	1	1	ĺ
(Tergitol Anionic 4)						
litanium dioxide (Titanox RA 40)	1					
Polyvinylpyrrolidone (protective		1	5			
colloid)						
int 0712					0.5	0.125

(1) Method of Preparation

The ingredients in Phase A were heated to 187°F; the ingredients in Phase B, minus the last three ingredients listed, were heated to 84°F. The Phase B mixture was added slowly to the Phase A mixture, which was stirred by the Dormey mixer. The resultant emulsion was stirred for 15 minutes. This batch of cream was split into six parts, and additives were blended into five of these samples as indicated in Table XIX.

(2) Physical Properties and Performance

	<u>ST-4</u>	ST-4A	ST-4B	ST-4C	ST-4D	ST-4E
Color	Slight yellow	Slight yellow	Very slight yellow	Slight yellow	Slight yel	low Slight yellow
Form	Cream	Cream	Cream	Cream	Cream	Cream
0dor	Very slight Aromatic	None	Nore	None	Minty	Slight Minty
Perfor	mance					
	<u>ST-4</u>	ST-4A	ST-4B	<u>ST-4C</u>	ST-4D	ST-4E
	thaw No change to 72 ⁰ F)	No change	No change	No change	No change	No change
Heat S	tab- Slight	Slight darken-	Slight			
ility	(155 ⁰ F) darken- ing	ing	darkening	Opales- cent		Not ested
Soil r	emoval Excell-	Excellent	Excellent	Excellent		xcell- nt

r. Effect of Addition of Hydrogenated Lanolin, Hexachlorophene, and a Nonionic Surfactant on Cleaner Properties

Hydrogenated lanolin, hexachlorophene and a nonionic surfactant were added to the product to determine the effect on the color and stability of the cream (Table XX).

TABLE XX

COMPOSITION OF CLEANER CONTAINING HYDROGENATED LANGLIN, HEXACHLOROPHENE, AND NONIONIC SURFACTANT

Identification

Phase A	Percent
Isoparaffinic hydrocarbon (Isopar H)	30
Light mineral oil	16
Glycerine	3
Lanolin, Hydrogenated (Super-Sat)	. 1
Stearic acid	8
Hexachlorophene	0.2
Phase B	
Mixed isopropanolamine	4
Distilled water	36
Alkyl phenyl polyethylene glycol ether	1
(Tergitol nonionic NPX)	
Polyvinylpyrrolidone	0.8

(1) Method of Preparation

Ingredients in Phase A were heated to $172^{\circ}F$ and stirred with a Dormey mixer. Ingredients in Phase B at $86^{\circ}F$ were added slowly to Phase A. The resultant emulsion was stirred for 15 minutes. This batch was split into two parts. One part was packaged warm $(140^{\circ}F)$; the other was packaged at $104^{\circ}F$. No difference in handling was observed in the packaging of the creams at $140^{\circ}F$ and $104^{\circ}F$.

The Phase A mixture was tinted yellow because of the hexachlorophene. The resulting emulsion had a light yellow color.

(2) Physical Properties and Performance

Physical properties

Emulsion type	0i1/Water
Performance	
Freeze-thaw (-26°F to 74°F)	No change
Heat stability	Darkened
Shelf stability (one month)	No change

s. Effect of Colorless Hexachlorophene

A fresh sample of hexachlorophene was used in other creams to determine if the color could be improved.

The emulsion described in paragraph 5r (Page 29) was yellow in color. In this batch, fresh, white hexachlorophene was used and the resultant color was white (Table XXI).

TABLE XXI

COMPOSITION OF CLEANER WITH COLORLES' HEXACHLOROPHENE

Phase A	Percent
Isoparaffinic hydrocarbon (Isopar H) Light mineral oil	30 16:
Hydrogenated lanolin (Super-Sat) Glycerine	1 3
Stearic acid Hexachlorophene	8 0.2
Phase B	
Mixed isopropanolamine	4
Distilled water	36
Sodium tetradecyl sulphate (Tergitol Anionic 4)	1
Polyvinylpyrrolidone	0.8
	100.0

(1) Method of Preparation

The hexachlorophene was dissolved in molten stearic acid and the mixture added to the remainder of the ingredients in the Phase A mixture which had been heated to 176°F. The ingredients in the Phase B portion were mixed and heated to 131°F. and were then added slowly to the Phase A portion while being stirred with the Dormey mixer. The resulting emulsion was mixed for 15 minutes and packaged at 113°F.

(2) Physical Properties and Performance

Physical Properties

Color	White
Ferm	Cream
Odor	Slight-agreeable
pН	7 🗜
Performance	

Freeze-thaw (-30°F. to 76°F.)

No change Heat stability (155°F.) Darkened slightly To lower the pH, 0.8g. of boric acid was mixed into 50 grams of this emulsion. The pH was lowered to 5; however, the viscosity was lowered appreciably. After five freeze-thaw cycles, the emulsion separated. The pH was lowered to 7.0 when 0.2 gram P_2O_5 was added to 50 grams of the emulsion. The viscosity was also lowered. This composition withstood 5 freeze-thaw cycles.

t. Effect of Various Amounts of Lanolin, Glycerine and Stearic Acid

A series of creams containing different quantities of lanolin, glycerine, and different grades of stearic acid was prepared to determine the effect on the physical properties of the cream (Table XXII).

COMPOSITION OF CLEANERS WITH DIFFERENT AMOUNTS OF MINOR COMPONENTS

Identification	SH-103	SH-105	SH-107	SH-109	SH-111	SH-113
Phase A			Percent			
Isoparaffinic hydrocarbon (Isopar H) Lt. mineral oil Lanolin Glycerine Stearic acid Hexachlorophene (1) Slightly Yellow Commercial (2) Mixture of 50% Commercial (1) and 50% Chemically Pure (3) Neo Fat 18 (4) Anhy. Lanolin U.S.P.	30 16 1 (4) 3 8 (1) 0.2	31 16 - 3 8 (2) 0.2	33 16 1 (4) - 3 (3) 0.2	34 16 - 8 (3) 0.2	30.8 16 1 3 8 (3) 0.2	30 16 1 3 8 (3) 0.2
Phase B						
Mixed isopropanolamine Distilled water Sodium tetradecyl sulphate (Tergitol Anionic 4)	4 36 1	4 36 1	4 36 1	4 36 1	4 36 1	4 36 1
Polyvinylpyrrolidone	$\frac{0.8}{100.0}$	$\begin{array}{c} 0.8 \\ 100.0 \end{array}$	$\frac{0.8}{100.0}$	$\frac{0.8}{100.0}$	$\tfrac{0.8}{100.0}$	$\begin{array}{c} 0.8 \\ 100.0 \end{array}$

(1) Method of Preparation

The hexachlorophene was dissolved in molten stearic acid and this mixture was added to the remainder of the ingredients of Fhase A and heated to 145-174°F. The ingredients in Phase B were heated to 120-138°F and added slowly to the Phase A mixture, which was stirred with the Dormey mixer. After the emulsion had formed, it was stirred for 15 minutes to achieve a smooth cream. The creams were packaged at 104-134°F.

(2) Physical Properties and Performance

Physical Properties	SH-103	SH-105	SH-107	SH-109	SH-111	SH-113
Composition Consistency	Light	Light	Light	Light	Light	Light
Workability	Good	Good	Good	Good	Good	Good
	1/Water	Oil/Water	Oil/Water	Oil/Water	Oil/Water	Oil/Water
pH	7.0	7.0	7.0	7.0	7.0	7.0
Soil Removal	Good	Good	Fair	Fair	Fair	Good
Odor	Slight	Slight	Slight	Slight	Slight	Slight
Color	Light	White	Slight	White	Slight	White
	Tan		Yellow		Yellow	,,,,,,
Form	Cream	Cream	Cream	Cream	Cream	Cream
Performance						
Identification						
Freeze Thaw (-40°F	No	No	Slight	No	No	No
to 76°F)	Change	Change	Separa- tion	Change .	Change	Change
Heat Stability (155°F)	Dark-	No	Broke	oke	Slightly	Slightly
	ened	Change			Darkened	Darkened
Heat Stability (155°F)	Very	No	Slightly	No	Slightly	Very
	Slightly	Change	Yellow	Change	Yellow	Slightly
I	arkened	-		J		Yellow

*Note: Samples were first exposed to five freeze-thaw cycles, followed by 5 heat cycles.

u. Laboratory Preparation of Resin-Based Waterless Hand Cleaners (W-1)

One of the tasks in this study was to investigate and to evaluate resinbase cleaners for the removal of soil. One such cleaner is described by U.S. Patent 2383610, dated 28 August 1945. This hand-clearing solution is applied to the hands and rubbed until all parts are coated. When the solvents evaporate, the remaining solids form a spongy mass which can be removed from the hands along with the soil without the use of a towel. Such cleaners are called waterless-towelless hand cleaners. A patented cleaner illustrating this product has the following composition:

Polyvinyl alcohol (PVA)	4.2%
Glucarine B (mannitol glycerol monooleate)	3.1
Tetrasodium phosphate (NA ₄ P ₂ 0 ₇ .10H ₂ 0)	0. 01
Trisodium phosphate (Na ₃ PO ₁ .12H ₂ O)	0.05
Trisodium phosphate (Na ₃ PO ₄ .12H ₂ O) Nacconol NR (monoalkylate derivative of aromatic monosulphate)	0.12
Lysol (Cresylic acid germicide)	0.91
Distilled water	91.6
	99.99

A modification of the patented product was prepared as follows: 50 grams of PVA (4% aqueous solution having a viscosity of 55-56 cp.) were dissolved in 1000 cc of distilled water heated to $180\text{--}200^{\text{O}}\text{F}$. Thirty cubic centimeters of Span 80 (sorbitan monooleate) was used instead of Glucarine B, which is no longer available. In 100 cc of distilled water, 0.1g. tetrasodium phosphate, 13g. Nacconol 4CF. (blodegradable successor to Nacconol NR), and 0.6g. trisodium phosphate were added and dissolved. The two solutions were mixed and 10 cc of Lysol was added. This solution was watery and separated into two phases on standing after exposure to a temperature of -26°F. A gel formed that persisted when the product reached room temperature. This gel retained its shape, but exhibited syneresis (exuded a liquid). Soil removal of the gelled mixture was poor. In an effort to increase the viscosity of the mixture, additions of 2.5 percent and 5.0 percent Cab-o-Sil M5 were made to 100 cc portions. Thicker mixtures were obtained, but on freezing at -26°F and thawing to room temperature, both mixtures formed gels. This product could not be thickened by the addition of more polyvinyl alcohol because of its limited solubility in water (4% @ 68°F).

Milton A. Lesser describes (31) a towelless, waterless hand cleaner with the following composition:

Ingredient	Parts by Weight
Colloresin 4000	14.3
Alcohol	5.5
Lanolin	0.3
Glycerine	5.5
Menthol Menthol	.0.1
Propyl para-hydroxybenzoate	0.3
Distilled water	74.0

Both J.I. Jones $^{(32)}$ and S.L. Collier $^{(33)}$ describe a simple water solution of polyvinyl alcohol which, when rubbed on the hands for a few seconds, will dry and then peel off, removing dirt and grease. The use of a 10 percent solution is suggested. Prior to World War II, polyvinyl alcohol was sold in Germany and proved to be popular as a hand cleaner with motorists and mechanics.

A series of experime all creams, prepared by Purdue University, have rolling properties and can be removed from the hands by rubbing, thus eliminating the need for towels. All the ingredients except the lanolin and water were mixed in the kerosene and heated to $482^{\circ}F$, at which time the lanolin was added. This mixture was removed from the heat source and water was added slowly. Constant stirring was continued until a firm gel was formed (Tables XXIII and XXIV).

FORMULATIONS OF WATERLESS HAND CLEANERS (ROLLING TYPE)
(Ingredients in gms. or mil)

Ingredients	17	18	19	20	21	22	23	24
Kerosene	60	55	50	50	50	55	60	30
Polyoxyethylene sorbitan trioleate (Tween 85)					5	5	5	
Polyoxyethylene sorbitan monooleate (Tween 80)					15	15	15	
Stearic acid	15	15	15	15	15	15	15	15
Triethanolamine	2	2	3	3	2	2	2	
Hexachlorophene (G-11)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
Distilled water Glyceryl monostearate Polyvinyl alcohol	20	20	20	20	35	35	35	50 4 6
Sorbitan sesquioleate (Arlacel C)								10
Stability Test (14°F. to 122°F.)	c	c	0,s	c	1	1	1	NS

Legend

- 0 No Separation
- c Large Separation
- s Stable
- 1 Liquefaction
- NS Not Suitable for Testing

An addition of a methyl and ethyl cellulose and paraffin was made at Purdue University to improve the flaking properties. These products were exposed to stability tests at 14°F. and 122°F. None of these combinations were considered to be acceptable products.

FORMULATIONS OF WATERLESS HAND CLEANERS (FLAKING TYPE)

(Ingredients in Grams or Mil)

Formula No.	25	26	27	28	29	30	31	32
Mc_hylcellulose (Methocel 4000 cps 50% sol.)			15	15				
Kerosene	60		60	15	10	60	60	60
Polyoxyethylene sorbitan monooleate (Tween 80)	20		20	15		15	15	15
Hexachlorophene	0.5	., .	0.5	0.5		0.5	0.5	0.5
Distilled water	20	75	16	16	75	25	2 5	25
Paraffin USP		22.5			22.5			
Sorbitan monostearate (Span 60)	1.25				2.50			
Polyoxyethylene sorbitan monostearate (Tween 61)	1.25				1.25			
Polyoxyethylene sorbitan trioleate (Tween 85)				5				
Ethylcellulose Ethylcellulose solution*						5 5	5 9	5 18
Stability (14° to 122°F.)	NS	С	b	b	С	a,s	O	c

Legend

- 0 No separation
- a Slight Separation
- b Moderate Separation
- c Large Separation
- s Stable
- NS Not Suitable for Testing

*Ethylcellulose Solution Ethylcellulose 5 gm. Alcohol USP 51 cc.

Mix with the electric mixer until a clear solution is effected. Then add the required amount of this ethylcellulose solution to the kerosene mixture and heat to $482^{\circ}F$.

7. Paper Towels

To remove the soil and excess cleaner from the hands, paper towels or cloths are required. Therefore, the OCD Sanitation Kit should contain some wiping material. In this study, paper towels conforming to Federal Specification UU-T-591, FSN 8540-262-7178, were found to be satisfactory. These towels are packaged in a carton containing 7500 and are priced at \$5.00. One towel is required for the removal of an average 1/16-ounce application of waterless hand cleaner; this will require 256 towels for each pound of waterless cleaner.

8. Bactericidal Properties, Skin Sensitization and Fungistatic Properties

Formula #145, waterless hand cleaner, containing 0.5% hexachlorophene, was tested at Purdue University for microbial inhibitory properties. The sample was diluted 1-5, 1-25, and 1-125 with sterile double distilled water. Using the disc method and the organisms common to the skin, such as Staphylococcus aureus 221, Staphylococcus albus 221, and Sarcina lutea 221, positive inhibitory effects were obtained, even at a dilution factor of 125. To determine the rate of action, a test at the 1-5 dilution ratio indicated that a one-minute exposure was adequate to produce bacteriocidal effect.

Skin sensitization studies were also performed at Purdue University. The patch test as modified by $Ward^{(30)}$ was employed on seven male and three female volunteers. Approximately 250 milligrams of formula #145 cream were placed on Band-Aids which, in turn, were put on the under surface of the upper arm. After 24 hours, the patches were removed and the area cleansed with alcohol to remove residual cream, and the skin was examined for redness or irritation after 15 minutes. A commercial cream known to be non-irritating was used as a control. In all cases except one, the results were completely negative. The exception, a female subject, reported she had a history of hypersensitivity to chemical agents.

The Fungicides and Germicides Laboratory of NLABS evaluated, for fungal resistance, SH-101, containing 0.2% hexachlorophene; SH-117, containing no hexachlorophene; #56 said to contain bithional; and #69 said to contain hexachlorophene. A mixed culture plate test (ASTM D1924-62) and a tropical chamber exposure test were performed. The mixed culture contained Aspergillus niger, flavus and versicolor, Penicillium funiculosum, Trichoderma sp., and Pullaria pullalans, as required by the standard method, plus Chaetomium globosum. Samples of SH-101 and SH-117 developed heavy fungal growth in one week in the plate test and luxuriant growth after three weeks. After four weeks in the tropical chamber, at Natick, both products developed fungal colonies. These tests indicate that this product without a fungicide will support the growth of fungi and that hexachlorophere is not a fungicide. Number 56 showed slight growth at the periphery of the plate smear after one week, but the growth did not increase during an additional two weeks of incubation; after two months exposure in the tropical chamber there was no growth when examined microscopically. The fungistatic property is attributed to bithional (2.2' thio bis (4,6 dichlorophenol fungicide. Number 69 developed moderate growth after one week and heavy growth after three weeks incubation; in the tropical chamber growth developed after two months. These results also showed that hexachlorophene is not a fungicide.

The same four creams were tested microbiologics .y in a commercial laboratory by the technique cited in Federal Specification F-H-3la,, Hand Cleaner. The results on various organisms were as follows:

		Inhibiti	on of Growth	in Millimeters
Organism	<u>#56</u>	#69	SH-113	SH-117
Staphylococcus aureus (Gram Positive)	45	6	3	0
Salmonella typhosa (Gram Negative)	0	0	0	0
Pseudomonas aeruginosa (Gram Negative)	., 0	0	0	0
Trichophyton mentagrophytes (Fungus)	0	0	2	0

These results show that the commercial cream #56, containing bithional, was effective against the Gram-positive Staphylococcus aureus, but not against the Gram-negative bacteria or the fungus. The hexachlorophene-containing creams (#69 and SH-113) were effective against the Gram-positive bacteria and SH-113 was effective against one of the fungi. SH-117, which did not contain a germicide or fungicide, showed no inhibition as expected. Hexachlorophene is not effective against Gram-negative bacteria. These results also show that more than 0.2 percent, and authorities state that a minimum of 0.5 percent of hexachlorophene is required in a cream of this type to insure bactericide properties against Gram-positive bacteria.

9. Packaging

The General Equipment and Packaging Laboratory, NLABS recommended that the cleaner be packaged in a one-pint-capacity metal can conforming to type III, exterior coating plan B, of Federal Specification PPP-C-96. This is a round, open-top can with double-seamed ends and a key-opening band reclosure feature. Blackplate, terneplate, or 0.25-pound electrolytic timplate shall not be used. The seaming compound shall not affect or be affected by t's hand cleaner or any of the components of the hand cleaner. As an alternative to the compound-lined, double-seamed ends and sides, the seams may be soldered.

10. Summary

The prime purpose of this study was to develop a hand cleaner that is stable under the temperature extremes encountered in the United States. Waterless hand creams are usually emulsions by nature, and are unstable and tend to break or separate when frozen or heated. The Earth Sciences Laboratory, NLABS advised that design conditions should include resistance to $155^{\circ}F$ for 4 hours, peaking at $160^{\circ}F$ for not more than one hour ,and to $-40^{\circ}F$ for 4 hours in unheated or outdoor shelters in the United States. Based on this advice, temperature resistance tests were conducted on the most promising products at $-40^{\circ}F$ and $155-160^{\circ}F$; these temperature extremes are more drastic than those required in the current Federal Specification ($14^{\circ}F$ and $122^{\circ}F$).

The type of soil used for the evaluation of a hand cleaner of any type is always a controversial subject. For the evaluation of the cleansing ability of the cleaners studied, a soil prescribed in the current Federal Specification was used, primarily because of its long accepted usage.

The antimicrobial properties of the cleaner were developed by the incorporation of hexachlorophene in the product. The use of this bacteriocide in personal cleaning items is quite common and has wide acceptance. Tests made at Purdue University confirmed the inhibitory and bacteriocidal effects of hexachlorophene when present in the cream at a 0.5 percent concentration and at dilution ratios of 1-125 and 1-5, respectively.

Creams containing 0.5 percent hexachlorophene were found to be non-irritating to the skin when tested by the patch method. Emulsions of the hydrocarbon solvent-mineral oil-surfactant type were found to be non-irritating to the skin in extensive tests. (20)

Three commercial products (#53, #60 and #69) met the Office of Civil Defense minimum requirements of temperature stability and soil removal as established in this study. Samples #53 and #60 are emulsified lotions supplied under Federal Specification P-H-0031, Type I and Type II class 1. Neither are antimicrobial as required by OCD. The third product, Sample #69, is satisfactory as reported. (20)

Towelless cleaners gell on freezing and the resultant product is a poor soil remover. Pressurized commercial packaged creams can be dispensed easily at room temperature and soil removal is excellent. The dispenser action is sluggish below 70°F and the container must not be stored above 120°F. The retail cost is \$2.36 per pound, or almost six times a target cost of less than \$.40 per pound.

Several formulations, recommended by industry, particularly CM-2 and X127 (Table IV and Table VII), were found to meet the freeze-thaw test, and were excellent soil removers. However, these products darkened on ageing and had a slight kerosene odor.

Purdue University formulated a number of creams and lotions. Cream #145 (Table XVI) was said to be the most promising of these waterless hand cleaners. However, samples supplied to NLABS settled in the containers and separated during the freeze-thaw test (- 40° F to 78° F).

An inexpensive organic solvent, such as kerosene, is used in most waterless hand cleaners. Although it is possible to mask the kerosene odor with perfumes, the replacement of kerosene with an isoparaffinic hydrocarbon makes this unnecessary.

To simplify the manufacturing and to decrease the cost, the creams were not homogenized, although Purdue University did use an ointment mill in the manufacture of their creams.

11. Conclusions

An inexpensive waterless hand cleaner has been developed that is an effective cleaner and will withstand exposure to a freeze-thaw and to an elevated temperature. This waterless hand cleaner intended for inclusion in the OCD Sanitary Kit has a composition similar to that of SH-105 except that it contains 0.5 percent hexachlorophene instead of 0.2 percent. This cream has good soil removal properties, will withstand freeze-thaw and high temperature storage, is white in color, is neutral, does not irritate the skin, has germicidal qualities, is easy to manufacture, and requires inexpensive raw materials. To insure the germicidal qualities of this cream, and in line with published data, the quantity of hexachlorophene has been set at 0.5 percent.

Pertinent data concerning the recommended formulation are included in Table XXV.

TABLE XXV

COMPOSITION AND COST OF THE RECOMMENDED PRODUCT

Ingredient	Percent by Weight	Cost per Pound	Cost of Ingredient
Isoparaffinic hydrocarbon	31.0	\$.046	0.014
Light mineral oil	15.7	.097	0.015
Glycerine	3.0	.245	0.007
Stearic acid	8.0	.255	0.020
Hexachlorophene	0.5	1.88	0.009
Mixed isopropanolamine	4.0	.500	0.020
Distilled water	36.0	.001	0.0004
Sodium tetradecyl sulphate	1.0	.500	0.005
Polyvinylpyrrolidone	0.8	.550	0.004
	100.0		$\overline{0.0944}/1b.$

Pertinent Physical Data

Freeze-Thaw $(-40^{\circ}\text{F} \text{ to } 78^{\circ}\text{F})$ - No change Heat stubility $(155^{\circ}\text{F}-160^{\circ}\text{F})$ - No change Residual effect on skin - Does not leave skin greasy

Paper towels, FSN 8540-262-7128, conforming to Federal Specification UU-T-591, at a cost of \$0.0067 each, in cartons of 7500, are recommended for inclusion in the kit for the removal of the loosened dirt and excess cleaner.

Requirements of the waterless hand cleaner for inclusion in the OCD Sanitary Kit will be included in a proposed specification.

12. References

- 1. Contract No. DA-19-129-AMC 1058(x)
- 2. Anon., Drug and Cosmetic Industry, 74, 93 (January 1954)
- 3. Anon., Drug and Cosmetic Industry, 81, 109 (July, 1957)
- 4. Anon., Drug and Cosmetic Industry, 67, 625 (November, 1950)
- 5. Anon., Drug and Cosmetic Industry, 68, 786 (June, 1951)
- 6. Anon., Drug and Cosmetic Industry, 69, 791 (December, 1951)
- 7. Anon., Drug and Cosmetic Industry, 65, 359 (September, 1949)
- 8. Anon., Drug and Cosmetic Industry, 62, 391 (March, 1948)
- 9. Anon., Drug and Cosmetic Industry, 79, 839 (December, 1956)
- 10. Anon., Drug and Cosmetic Industry, 59, 121 (July, 1946)
- 11. Anon., Amer. Perf. and Essent. Oil Rev., 49, 251 (March, 1947)
- 12. Anon., Amer. Perf. and Essent. Oil Rev., 49, 31 (July, 1947)
- 13. Anon., Amer. Perf. and Essent. Oil Rev., 50, 139 (August, 1947)
- 14. Wells, F.W. and I.I. Lubowe, "Cosmetics and the Skin," p. 258 Reinhold, New York, 1964.
- 15. Wells, F.W. and I.I. Lubowe, "Cosmetics and the Skin," p. 259 Reinhold, New York, 1964.
- 16. Atlas Powder Company, Wilmington, Delaware, "Drug and Cosmetic Emulsions," p. 24, 1946.
- 17. Union Carbide Chemical Corp., New York, "Emulsions and Detergents," pp. 71-72, 1948.
- Union Carbide Chemical Corp., "Emulsions and Detergents, pp. 67-68, New York, 1955.
- 19. Private communication from V.W. Glebus, Former Civil Defense Director of Natick, Mass., 31 May 1966.
- 20. Birmingham, Donald J. and Vernon B. Perone, U.S. Public Health Service, WADC Technical Report 55-467, "Evaluation of Waterless Hand Cleaners," Wright Air Development Center, January 1956.

- 21. Military Specification MIL-T-43007B, Towel, Paper, Cleansing Wet (Packet), 12 August 1965.
- Interim Federal Specification P-H-0031C (GSA-FSS), Hand Cleaner,
 Duplicating Ink; Hand Cleaner, Grease, 21 February 1966.
- 23. Walter, G. and Gump, W., "Effects of pH on Hexachlorophene" Sindar Corp.; Delawanna, J.J. Soap and Chemical Specialties, July, 1963.
- 24. Technical Bulletin H-1, Sindar Corporation, 321 West 44th Street, New York 36, New York (Feb. 1962).
- 25. Cruse, M.N. and Miller, D.L., "Waterless Hand Cleaners," The Dow Chemical Company, Midland, Michigan., Soap and Chemical Specialties, Nov., 1963
- Letter to George J. Merritt, NLABS, from Marianna Hillegas, Atlas Chemical Industries, Wilmington, Delaware, 6 June 1966.
- 27. Letter to George J. Merritt, NLABS, from M. J. Smoleski, Humble Oil & Refining Company, Hutchinson River Parkway, Pelham, New York, 5 May 1966.
- 28. Technical Bulletin No. 80, The Baker Castor Oil Co., Bayonne, New Jersey, 1966
- 29. Private communication to Harry T. Skerritt, NLABS from N. J. Beach, Sugar Beet Products, 14 October 1966.
- 30. Ward, J.B., "A Study of Ion Exchange Resins as Carriers for Tropical Medication in a Film-Forming Base," p. 107, Ph.D. thesis, Purdue University, West Lafayette, Indiana, 1964.
- 31. Lesser, Milton A., Modern Chemical Specialties, McNair-Dorland Company, New York 1950.
- Jones, J.I., "Polyvinyl Alcohol, Its Chemistry and Application," Brit. Plastics, 16 77-80 I22-9 (1944).
- 33. Collier, S.L. PVA Polyvinyl Alcohol, Perf. & Cosmetics 21, 690-1, 695 (1948).

Note: Remove Appendix A prior to distribution outside the Department of Defense. APPENDIX A

IDENTIFICATION CODE OF WATERLESS HAND CLEANERS

Sample No.	Trade Name - Manufacturer
41	Drexall - Dreshler Product, Inc., Dreshler, Ohio
42	DIF - J. Nelson Preivitt, Inc., Rochester, N.Y.
43	PRESTO - Bond Sales Co., Pawtucket, R.I.
44	LAN-LIN - Radiator Specialty Co., Charlotte, N.C.
45	M & V HAND CLEANER - Mattage & Volger, Inc., Park Ridge, N. J.
46	KAR-KARE - Kar Kare Products Co., Cleveland, Ohio
47	QUKCKEE - B.T. Babbitt, Inc., New York, N.Y.
48	DL - SL Skin Care Products, Buffalo, N.Y.
49	FSN 8520-062-4319 - Amaza Laboratories, Cleveland, Ohio
50	FSN 8520-527-9942 - Gojer, Inc., Akron, Ohio
51	FSN 8520-082-2144 - Amaza Laboratories
52	FSN 8520-634-9040 - Gojer, Incorporated
53	FSN 8520-527-9940 - Amaza Laboratories
54	FSN 8520-082-2146 - G.H. Packwood, St. Louis, Missouri
55	FSN 8520-082-2146 - Hanlon Chemical Co., Kansas City, Missouri
56	FSN 8520-225-8563 - Hanlon Chemical Co., Kansas City, Missouri
57	FSN 8520-965-2108 - Hanlor Chemical Co., Kansas City, Missouri
58	FSN 8520-965-2107 - Hanlon Chemical Co., Kansas City, Missouri
59	FSN 8520-782-2183 - Hanlon Chemical Co., Kansas City, Missouri
60	Duplicating ink cleaner - Nowlon Company, Fort Worth, Texas
61	Hand Cleaner - Fed. Spec. P-H-31a, Type II, Class I, Mfg. Unknown
62	Liquefying Cleansing Cream - Colgate-Palmolive, Jersey 13-24, N.J.

APPENDIX A (cont'd)

Sample No.	Trade Name - Manufacturer
63	Viking Waterless Hand Cleaner - Viking Mfg. Co., Natick, Mass.
64	VY Kreme - Viking Mfg. Co.
65	PAX-SOLV - G.H. Packwood Mfg. Company
66	Citroen - Thatcher Chemical Research, San Gabriel, Calif.
67	Sno Hand Cleaner - Thatcher Chemical Company
68	Waterless Hand Cleaner - P-H-3la - Purchased by the Office of Civilian Defense.
69	Paxit, G.H. Packwood Mfg. Co.
70	Boraxo Waterless Hand Cleaner, U.S. Borax & Chemical Corp.,
L.A. Cal; N.Y.	

Note: Remove Appendix A prior to distribution outside the Department of Defense.

APPENDIX B

MATERIAL SOURCES

Isopar H - Humble Oil & Refining Co. Houston, Texas

Light Mineral Oil - Paraffin Oil N.F. - Viscosity 125/135 - Fisher Scientific Co. Fair Lawn, New Jersey

Glycerine - 99.5% U.S.P - Atlas Chemical Industries, Inc; Wilmington, Delaware 19899

Stearic Acid - Neo Fat 18, Flaked - Armour Industrial Chemical Company, 401 N. Wabash, Chicago, Illinois 60690

Hexachlorophene - G-11, Sindar, 125 Delawanna Ave., Clifton, N.J. 07014

Mixed isopropanolamine - Union Carbide Chemical Corp., 270 Park Ave., New York, N. Y. 10017

Sodium tetradecyl sulphate - Tergitol Anionic 4 - Union Carbide Chemical Corporation

Polyvinylpyrolidone - PVP-K30, General Aniline & Film Corp., 140 W. 51 St. N.Y., N.Y. 10020

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A waterless hand cleaner has been developed by the US Army Natick Laboratories for inclusion in the Civil Defense Sanitation Kit. This sanitation kit, which is described in "Description, Care, and Handling of Supplies for Public Fallout Shelters (OCD Manual 8520.1)," has an estimated storage life of at least five years. The contents of this kit must satisfy the sanitary requirements of occupants in Civil Defense shelters. The cleaner developed under this study to replace the current product is a paste emulsion of a mineral oil, a hydrocarbon solvent, an amine soap, a humectant, an anionic surfactant, a protective colloid, and a germicide. The cleaner shows good soil removal properties and good storage stability properties at room temperature as well as at -40 f. or -26 f. and 155-160 f. This cleaner has microbial inhibitory properties because of the action of the germicide, hexachlorophene. A key-opening band, reclosure-type round can made of hot dipped tinplate or 0.50 pound minimum electrolytic tinplate is recommended for packaging the cleaner. The seam sealing compound must be inert to the cleaner and the solvent.

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